A

Research Proposal on

Synthesis and Characterization of Metal (Ni and Fe) Oxide for various applications

For Registration to the Degree of Doctor of Philosophy

IN THE FACULITY OF SCIENCE

THE IIS UNIVERSITY, JAIPUR

Submitted By:

JYOTI YADAV

ICG/2017/24609

Under the Supervision of

Dr. RIMPY SHUKLA

Assistant Professor

DEPARTMENT OF PHYSICS

The IIS University, Jaipur

May, 2018

CONTENTS :

- Introduction of Nanotechnology
- Metal Oxide Nanomaterials
  - Importances
- Target Metal Oxide Nanomaterials
  - NiO
  - Fe_2O_3
- Application of Oxides
- Review of Literature
- Motivation/ Justificstion
- Research gap
- Objectives
- Research Methodology

  Methods of preparation of nanoparticles
  - Sol-gel Method
  - Hydrothermal Method
- Characterization techniques of nanoparticles
  - XRD
  - SEM
  - TEM
  - FTIR
  - UV-Vis Spectroscopy
  - VSM
- Plan of work
- References

1.Introduction of Nanotechnology

Nanoscience is an interdisciplinary field of the sciences of physics, chemistry and materials sciences, meant for the design and fabrication of nanomaterials and their application. This branch of science is meant to understand the fundamental physical and chemical properties and the phenomenon of nanomaterials and nanostructures, and because of the novel application of nanomaterials, the science of nanomaterials has evolved as a frontline research area. Feynman pointed out the importance of nanotechnology at the annual meeting of the American Physical Society in 1959, in the classic science lecture entitled **‘‘There is plenty of room at bottom”**. In the last three decades, many discoveries and inventions have been made in the field of nanosciecne in terms of fabricating new materials and utilizing them for applications. Various new experimental techniques, with unique and desired properties of nanomaterials fabrication have been discovered.

Considerable research efforts with different synthesis methods have given brith to different class of nanomaterials, typically classified into three categories based on their dimensionality: 0 dimensional, one dimensional, two and three dimensional. Quantum dots and the individual molecules fall in the 0-dimensional structures where the nanoparticles are isolated from each other. One dimensional nanostructures where atleast one of the dimension goes in the range of nanoscale order are being highly utilized and have versatile application in the nanodevice fabrications. Thin nano films lie in the two dimensional structures and are studied extensively for the utilization of nanodevice application. Three-dimensional nanomaterials include powders, fibrous, multilayer and polycrystalline materials in which the 0D, 1D and 2D structural elements are in close contact with each other and form interfaces. An important type of three-dimensional nanostructured materials is a compact or consolidated (bulk) polycrystal with nanosize grains, whose entire volume is filled with those nanograins.

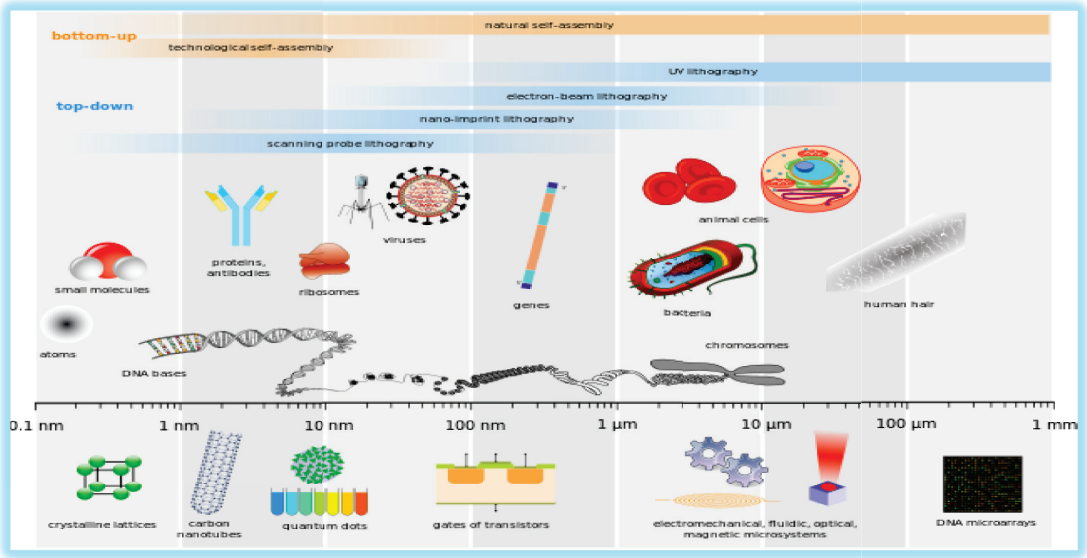


Figure1: Nanoscale according to size of materials

Almost all materials system including material, insulator and semiconductors show size dependent electronic or optical properties in the quantum size regime. Among these, the modification in the energy band gap of semiconductor is the most attractive one because of

the fundamental as well as technological importance. The band gap can be observed from the same material. Nanoparticles are becoming key components in a wide range of applications.

Research encompasses numerous disciplines, e.g. nanotechnology, molecular engineering, medicine, pharmaceutical drug manufacture, biology, chemistry, physics, optical components, polymer science, mechanical engineering, toxicology, cosmetics, energy, food technology and environmental and health sciences.

2. Metal oxide nanomaterials

Metal oxides because of their electronic structure differences, exhibit metallic, semiconductor, or insulator character. Preparation of these materials through the novel synthesis procedures can be described as physical and chemical methods. In general, two approaches have been used for the synthesis of these metal oxide nanostructures, top-down and bottom-up fabrication techniques. These approaches involve liquid–solid or gas–solid transformations. Metal oxide nanostructures among the most versatile groups of semiconductor nanostructures stand out as one of the most common, most diverse and most probably richest class of materials due to their extensive structural, physical and chemical properties and functionalities. In recent times metal oxides have been at the heart of many dramatic advances in the materials science. These materials display most fascinating and widest range of properties.

Due to the unique and tunable properties of these metal oxides such as optical, optoelectronic, magnetic, electrical, mechanical, thermal, catalytic, photochemical etc. made themselves excellent candidates for various high level technological applications. For instance, fuel cells, secondary battery materials, ceramics, chemical sensors, gas sensors and biosensor, solar cells, alkaline and lithium ion batteries, pyroelectric, piezoelectric, ferroelectric, magnetic, actuator, super capacitors, optical devices, lasers, waveguides, infrared(IR) and solar absorbers, gate dielectric, dielectrics in dynamics random access memories, High TC superconductivity, decoupling capacitors, magneto- resistance and so on. Hence metal oxide nanostructure materials have been actively studied in a broader perspective by the researchers. Therefore it is essential to explore its understanding in great details interms of their synthesis, properties and applications.

2.1 Importance of Metal Oxide Nanostructures

Nanoparticles of metal oxides have attracted increasing technological and industrial interest due to the changes in their optical, magnetic, electrical and catalytic properties accompanied with improved physical properties of stability or chemical passivity. Many physical properties of nanoparticles differ drastically from that of a single crystal of the same chemical composition. At nanoscale size, due to the confinement effect of electronic states and large number of surface atoms, many physical properties are influenced compared to their bulk phases.

Metal oxide nanoparticles have technological applications in areas such as catalysts, passive electronic components and high performance ceramics. These materials play important role in the selective surface modification of different substrates in the form of coatings. In comparison to that of bulk metaloxide phase nanomaterial metal oxides contain large fraction of

total atoms as surface atoms, which makes a distinct contribution to the free energy and results in the large changes in the thermodynamic properties (melting temperature depression, solid-solid phase transition elevation). Also the intrinsic properties of metal oxide are transferred by quan-tum size effect, that is changes in the optical and electrical properties with size arises because of the transformation in the density of electronic energy levels.

2.2 Target metal oxide nanomaterials

1. Nickle oxide (NiO):

Nickel is a strong, lustrous, silvery-white metal that is a staple of our daily lives and can be found in everything from the batteries that power our television remotes to the stainless steel that is used to make our kitchen sinks. Nickel oxide catches much intension due to its unique physical and chemical stability. Nickel oxide with chemical formula NiO found rarely in nature as bunsenite mineral form.

As like all other transition metal oxide, nickel oxide has been especially investigated in the degradation of several environmental pollutants & due to its properties, the interest in NiO as a photocatalyst has increased. Nickel oxide appears to be especially efficient as catalyst for wastewater pollution abatement. Nickel oxide based materials proved to be more effiecient for photocatalytic degradation of dyes. In brief, nickel oxide nano particles have received significant attention in the recent years for various applications.

Nickel is a Block D, Period 4 element, while oxygen is a Block P, Period 2 element. Nickel oxide nanoparticles appear in green powder form, and are graded as very toxic. They can cause an allergic skin reaction, prolonged harmful effects to aquatic life, and possible damage to organs due to prolonged or repeated exposure.

Chemical Properties:

Table:1 Properties of Nickel Oxide Nanoparticles

Chemical symbol	NiO
CAS No.	1313-99-1
Group	Nickel 4 Oxygen 16
Electronic configuration	Nickel [Ar]$3d^8$ $4s^2$
Nickel	78.55
Oxygen	21.40

Physical Properties:

The physical properties of nickel oxide nanoparticles are given in the following table.

Density	6.67 g/cm^3	0.240 lb/in^3
Molar mass	74.71 g/mol	-

Thermal Properties:

The thermal properties of nickel oxide nanoparticles are provided in the table below.

Melting point	1955°C	3551°F

2. Iron Oxide (Fe_2O_3) :

Iron oxides are chemical compounds composed of iron and oxygen. All together, there are sixteen known iron oxides and oxy-hydroxides. Iron oxide NPs are found naturally in the environment as particulate matter in air pollution and in volcanic eruptions. Either magnetite or maghemite – the two most commonly studied iron oxides − particles can be generated as emissions from traffic, industry and power stations but can also be specifically synthesised chemically for a wide variety of applications (so-called engineered nanoparticles). Iron oxides play an important role in many geological and biological processes, and are widely utilized by humans, e.g., as iron ores, pigments, catalysts, in thermite , Hemoglobin. Common rust is a form of iron(III) oxide. Iron oxides are widely used as inexpensive, durable pigments in paints, coatings and coloured concretes.

Although Iron oxide is found in nature in different forms, Magnetite (Fe_3O_4), Maghemite (γ-Fe_2O_3) and Hematite (α-Fe_2O_3) are the most common among them.

Iron oxide magnetic nanoparticles differ with their atoms and bulk counter parts in their physical and chemical properties. As each nanoparticle is considered a single magnetic domain, large surface area and quantum size effects lead to some dramatic change in magnetic properties resulting in super paramagnetic phenomena and quantum tunnelling of magnetization. Based on their unique physical, chemical, thermal and mechanical properties, super para-magnetic nanoparticles offer a high potential for different applications. These applications demand nanomaterials of specific sizes, shapes, surface characteristics, and magnetic properties, fields of high- density data storage, ferrofluids, magnetic resonance imaging, waste water treatment, bio separations and biomedicines.

Table:2 Properties of Iron Oxides

Chemical symbol	Fe_2O_3
Group	Oxygen 16 Iron 8
Electronic Configuration	Iron[Ar] $3d^6$ $4s^2$ Oxygen[He] $2s^2 2p^6$
Element	Content(%)
Iron	69.93%
Oxygen	30.06%
Density	5.34g/cm3
Boiling point	1,897ºc
Melting Point	1,566ºC
Physical properties	
Metric	Imperial

Molar Mass 1.569g/mol	-
Solubility in water	Insoluble
Solubility	Soluble in diluted acids
Cordination geometry	Octahedral
Odour	Odourless
Appearance	Red-brown solid

.

2.3 Application Of Target Oxides

Iron oxide (Fe_2O_3) has a range of applications such as:In magnetic resonance imaging to provide enhanced contrast at very low concentrations in the nanomolar range for studying tumors. As a targeted delivery vehicle and as a drug delivery coating for nanoscale anti-cancer drugs.For magnetic data storage In coatings, plastics, nanowires, nanofibers, and textiles and in specific alloy and catalyst applications.For Magnetic Resonance Imaging (MRI) As drug carriers for target specific drug delivery As gene carriers for gene therapy As therapeutic agents for hyperthermia based cancer treatments As magnetic sensing probes for in-vitro diagnostics (IVD) As Nanoadjuvant for vaccine and antibody production.Magnetite and maghemite are preferred in biomedicine because they are biocompatible and potentially non-toxic to humans. Iron oxide is easily degradable and therefore useful for in vivo applications. Results from exposure of a human mesothelium cell line and a murine fibroblast cell line to seven industrially important nanoparticles showed a nanoparticle specific cytotoxic mechanism for uncoated iron oxide. Solubility was found to strongly influence the cytotoxic response. Labelling cells (e.g.stem cells, dendritic cells) with iron oxide nanoparticles is an interesting new tool to monitor such labelled cells in real time by magnetic resonance tomography.

Nickel oxide (NiO) has a range of applications such as:For making electrical ceramics such as thermistors and varistors e.g. ferrites (nickel zinc ferrite). In Pigments for ceramic, glasses and glazes. Nickel oxide can be reacted with acids to form salts and other compounds e.g. nickel sulfamate for electroplating and nickel molybdate for hydrodesulfurisation catalysts. Gold doped nickel oxide films can be used as transparent electrodes in optoelectronic device. In lithium nickel oxide cathodes for lithium ion microbatteries. In electrochromic coatings, plastics and textiles, nanowires, nanofibers and specific alloy and catalyst applications. As a catalyst and as anti-ferromagnetic layers. In light weight structural components in aerospace, adhesive and coloring agents for enamels.In active optical filters, automotive rear-view mirrors with adjustable reflectance, in cathode materials for alkaline batteries, Electro chromic materials, energy efficient smart windows. Materials for gas or temperature sensors, such as CO sensor, H_2 sensor, and formaldehyde sensors

3. Review Of Literature

Sharma et al [2018] determined Nickel oxide has been synthesized by solution combustion technique. The nickel oxide ceramic was annealed at 600°C and 1000°C for 2 hours. Structural, electrical, dielectric and magnetic properties were analyzed which are strongly dependent upon the synthesis method. Structural properties were examined by X-ray diffractometer (XRD), which confirmed the purity and cubic phase of nickel oxide. XRD data reveals the increase in crystallite size and decrease in full width half maximum (FWHM) as the annealing temperature increases. Electrical conductivity is found to increase from 10^{-6} to 10^{-5} ($\Omega^{-1}cm^{-1}$) after annealing. Dielectric constant is observed to increase from 26 to 175 when the annealing temperature is increased from 600°C to 1000°C. Low value of coercive field is found which shows weak ferromagnetic behavior of NiO. It is observed that all the properties of NiO particulate improve with increasing annealing temperature.

Lassoued et al [2018] Studied the synthesized products have been studied by TGA, Differential Thermal Analysis (DTA), X-ray diffraction (XRD), Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Fourier Transform Infra-Red (FT-IR), Raman spectroscopy, Ultraviolet–Visible (UV–Vis) analysis and Vibrating Sample Magnetometer (VSM). The TGA showed three mass losses, whereas DTA resulted in three endothermic peaks. XRD measurements confirm that all the prepared nanocrystals consist only in nanocrystalline hematite phase. TEM and SEM show that the size of the nanoparticles decreases with Ni-doping. FTIR and Raman spectroscopies confirm the phase purity and the phonon modes of the synthesized nanoparticles. The UV–Vis absorption measurements confirm that the decrease of particle size is accompanied by a decrease in the band gap value from 2.02 eV for α-Fe_2O_3 down to 1.81 eV for 8 mol% Ni-doped α-Fe_2O_3.

Khan et al [2017] Studied Haematite (Fe_2O_3) nanorods are synthesized by reflux assisted coprecipitation method in two steps. In the first step, spherical nanoparticles of ferric oxyhydroxide (FeOOH) are synthesized. In the second step, FeOOH nanoparticles are converted into Fe_2O_3 nanorods by calcination of 4 h. These products (FeOOH and Fe_2O_3) are subjected to x-ray diffractometry to analyze their lattice structure, lattice parameters, diffraction planes and miller indices. Both of these products are also subjected to scanning electron microscopy (SEM) and transmission electron microscopy (TEM) to analyze their morphology. SEM and TEM observations have revealed that products are monodisperse and hollow. The dimensions of FeOOH nanoparticles and Fe_2O_3 nanorods are also measured from SEM and TEM observations. The heat transport properties of FeOOH are compared with that of Fe_2O_3. The value of thermal conductivity, thermal diffusivity and specific heat of FeOOH and Fe_2O_3 are measured to analyze their heat transport/storage characteristics. These products are also used as fuel additive.

Riasat et al [2016] Studies the hollow spheres of iron oxide (α-Fe_2O_3) were successfully synthesized synthesis by using hydrothermal method. Iron salt was dissolved together with glucose in water and then the mixture was heated to 180ºC in an autoclave at 12 and 24 hours of synthesis time separately. Hollow α-Fe_2O_3 spheres of around 200 to 300 nm size were formed after the calcination that lead to the removal of carbon. Increasing the reaction time will decrease the shell thickness. Phase confirmation and crystalline structure of these nanoparticles were done by XRD. Surface morphology was characterized by SEM and TEM analysis showed the hollow spheres inside and a shell of α-Fe_2O_3.

Manisha et al [2016] Studied Nickle oxide (NiO) nanoparticles have been synthesized via modified Sol-gel method. In this modified method, oxalic acid was replaced with citric acid which was mixed with ethylene glycol to form a homogenous gel and replaced ethyl alcohol with ethylene glycol. The metal nanoparticles were characterized by XRD, UV-Vis and FT-IR spectroscopy. The results obtained from XRD, UV-Vis and FT-IR spectra analysis confirms the formation of nickle oxide nanoparticles.

Mirzaei et al [2016] Studied Fe_2O_3 nanoparticles (NPs) have been synthesized by using a sol-gel method from iron nitrate, citric acid as complexing agent and ethylene glycol as polymerization agent. The calcined Fe_2O_3 NPs were fully characterized by different techniques. It was confirmed that ultrafine and highly crystalline Fe_2O_3 NPs with high purity and mesoporous nature can be obtained after calcination at 550 °C for 3 h. In addition, the results of electrical resistance measurements of the fabricated Fe_2O_3 thick films showed that Fe_2O_3 thick films have stable electrical properties which are beneficial for electrical applications such as gas sensing and field effect transistors.

Dang et al [2015] Studied the NiO p-type semiconducting nanowires with polycrystalline structure were prepared by a facile and scalable hydrothermal method. Morphology and crystal structure of the NiO nanowires were investigated by scan electron microscopy, X-ray diffraction, and transmission electron microscopy. The nanostructured material was then tested as hydrogen sensor showing very good performance in terms of sensor response, stability, absence of drifts, and speed of response and recovery.The selectivity of the NiO sensor to hydrogen towards other gases (ethanol, ammonia, and liquefied petroleum gas) was found to be good.

Rahdar et al [2015] Studied the Nanostructured NiO were synthesized by co-precipitation method using Nickel(II) Chloride Hexahydrate ($NiCl_2.6H_2O$) and sodium hydroxide (NaOH) as starting material. Structural, optical and magnetic properties of nanostructures were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), Atomic force microscope (AFM), UV–Vis absorption; Fourier transformed infrared (FTIR) and vibrating sample magnetometer (VSM) technique. The X-ray diffraction pattern studies revealed the NiO have a face-centered cubic (FCC) structure and confirmed the presence of high degree of crystallinity nature NiO nanoparticles that their average size is found to be 26 nm. The composition of nanostructures confirmed by analysis of FTIR spectra. The average size of the NiO nanoparticle observed from scanning electron microscopy images is found to be dimensions about 24 nm. Magnetic measurement confirmed the Nickel Oxide nanostructures superparamagnetic behavior at room temperature (RT) after calcinations.

Marbella et al [2015] discuss recent developments in the application of NMR techniques to the study of noble metal nanoparticle growth, surface chemistry, and physical properties.

Shaker et al [2013] investigated Magnetite (Fe_3O_4) nanoparticles have been successfully synthesized by Sol–Gel method by using Ferric nitrate ($Fe(NO_3)_3.9H_2O$) and Ethylene glycol ($C_2H_6O_2$) as precursors in different annealing temperatures. The obtained nanoparticles have been characterized by X-Ray diffraction (XRD), Scanning Electron Microscope (SEM), X-ray energy dispersive spectrometer (EDS) and Particle Size Analyzer. XRD measurements

indicate that the obtained nanoparticles are single phase and the particle size increased by increasing the temperature. Environmental pollution such as dyes has been excessively released into the environment and has created a major global concern. Congo Red is a benzidine-based anionic diazo dye with two azo groups. It is toxic to many organisms and is a suspected carcinogen and mutagen. The presence of Congo Red (CR) in water even at very low concentration is highly visible and undesirable. Present work is focused on synthesis of magnetite nanoparticles which showed a high adsorption capacity of Congo Red and is useful in removal of CR from wastewater.

Cheng et al [2012] investigated the applicability of maghemite (γ-Fe_2O_3) nanoparticles for the selective removal of toxic heavy metals from electroplating wastewater. The maghemite nanoparticles of 60nm were synthesized using a coprecipitation method and characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectroscopy (EDX).

Rogojan et al [2011] studied by the sol-gel method, the synthesis started from different chemical nature precursors – inorganic (aluminum chloride, $AlCl_3$) and organic (aluminum triisopropylate, $(C_3H_7O)_3$)Al). The powders obtained after drying the gel were heat treated at 1000ºC and 1200ºC for 2 hours. X-ray diffraction was used in order to characterize the powders in terms of their crystallinity degree and crystallite size. Microstructural and morphological characterization was performed using electron-microscopic techniques - scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

Basavaraja et al [2011] Studied the nanometer-sized α -Fe_2O_3 particles have been prepared by a simple solvothermal method using ferric acetylacetonate as a precursor. The products were characterized by X-ray diffraction (XRD), energy dispersive X-ray microanalysis (EDAX), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transition electron microscopy (TEM), infrared spectroscopy (IR) and thermal analysis (TG–DTA). XRD indicates that the product is single-phase α -Fe_2O_3 with rhombohedral structure. Bundles of acicular shaped nanoparticles are seen in TEM images with an aspect ratio ~ 12; typically 8–12 nm wide and over 150 nm long. The α -Fe_2O_3 nanoparticles posses a high thermal stability, as observed on thermal analysis traces.

Changyu et al [2011] Studied the Mesoporous nanosheets of single-crystalline β-nickel hydroxide (β-$Ni(OH)_2$) were successfully synthesized via a facile hydrothermal method using $Ni(NO_3)_2$.$6H_2O$ as precursor in a mixed solution of sodium hydroxide (NaOH) and sodium dodecylbenzenesulfonate (SDBS). Single-crystalline nickel oxide (NiO) mesoporous nanosheets can be obtained through a thermal decomposition method using β-$Ni(OH)_2$ mesoporous nanosheets as precursor. The influences of SDBS and hydrothermal treatment were carefully investigated; the results showed that they played important roles in the formation of β-$Ni(OH)_2$ mesoporous nanosheets. The as-obtained β-$Ni(OH)_2$ and NiO were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), thermal gravity-differential thermal analysis (TG-DTA), and specific surface area, and pore size test.

Wenqing Qin et al [2010] Studied Single-crystalline α-Fe_2O_3 nanocubes were successfully obtained in large quantities through a facile one-step hydrothermal synthetic route under mild conditions. In this synthetic system, aqueous iron (III) nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) served as iron source and triethylamine served as precipitant and alkaline agent. By prolonging reaction

time from 1 h to 24 h, the evolution process of α-Fe_2O_3, from nanorhombohedra to nano hexahedron, and finally nanocube, was observed. The products were characterized by Powder X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Highresolution Transmission Electron Microscopy (HRTEM), Selected-Area Electron Diffraction (SAED), and Fourier Transform Infrared Spectrometry (FTIR)

4. Motivation /Justification

Nickel and Iron oxides has major applications. They exhibit magnetic properties. They are generally used for optical properties as pigments for paints, plastics, ceramic glazes and enamels, as photoelectric, recording materials, catalysts, sensors, ceramic materials etc. Other uses include oxygen sensors, photovoltaics and antimicrobial coatings, water purification. For making electrical ceramics such as thermistors and varistors. Magnetic properties of NiO nanoparticles with different sizes and at different temperatures are compared. The nickel oxide nanoparticles are mostly used in batteries like lithium ion batteries, nickel-iron battery, nickel-Zinc battery, nickel- cadmium battery etc. Iron oxide nanoparticles include terabit magnetic storage devices, catalysis, sensors, super paramagnetic relaxometry (SPMR), and high-sensitivity biomolecular magnetic resonance imaging (MRI) for medical diagnosis and therapeutics. Common rust is a form of iron(III) oxide. Iron oxides are widely used as inexpensive, durable pigments in paints, coatings and colored concretes.

4.1 Research Gap

In the above works review by us most of them have prepared the materials and recorded their properties by characterization. Some of them (Cheng.et al, Shaker.et al) have investigated the (Ni, Fe) oxide material for their application in water purification. However work on the removal of metallic ions (lead, copper, zinc etc.) are very limited. Therefore, there is a need for further research in this area.

The drinking water obtain from well, ponds it generally contain heavy metal ions which is mercury, cadmium, lead, copper, chromium, nickel, zinc etc. These metal ions cannot be detected by naked eye, smell or taste. For example mercury, cadmium, lead, copper, chromium, nickel, zinc etc. The source of heavy metals are – acidic rain ,detergent and refined petroleum products, industrial and consumer wastes, copper occurs in drinking water from copper pipes and algal growth. In current era, pH value measurement, thrmogravimetric analysis, differential scanning calorimetry and UV-Visible spectroscopy techniques are usually employed for detection and identification and identification of ionic impurities in water. Research on environmental health risks is also limited but suggests that multiphase metal oxide may have a minor adverse impact on human or environmental healthand further research is necessary to determine the impact.

Keeping in view of above exciting research area with fulfilling the gaps of available reviews, the proposed research will be very potential and innovative to scientists and engineers working in this field, particularly in purification of water.

5. Objectives

Scope of this work is focused on the following steps:

- To synthesize the NiO and Fe_2O_3 by using chemical synthetic methods (sol-gel method and hydrothermal method).
- To investigate various properties of the samples, it has to undergo a number of characterisation techniques. It is proposed to use the following techniques:
  - Crystals structure by using XRD diffraction patterns.
  - Particle size and crystalline nature by using Transmission Electron Microscopy.
  - Surface morphology by Scanning Electron Microscopy.
  - Optical properties by UV-Vis Spectroscopy.
  - Various characteristic functional groups in molecules of synthesized nanomaterial by FTIR spectroscopy analysis.
  - Magnetic properties by Vibrating Sample Magnetometer.
- To compare the properties of the samples of above materials obtain from sol-gel and and hydrothermal method.
- To investigate effect of temperature on Crystallographic phases and Morphologyof the sample.
- To find out optimum calcination temperature for the use of above materials in water treatment application.
-

6. Research Methodology

6.1 Methods of preparation of nanoparticles

1. Sol-gel Method:

The sol-gel process may be described as:

"Formation of an oxide network through polycondensation reactions of a molecular precursor in a liquid."

A sol is a stable dispersion of colloidal particles or polymers in a solvent. The particles may be amorphous or crystalline. An aerosol is particles in a gas phase, while a sol is particles in a liquid, A gel consists of a three dimensional continuous network, which encloses a liquid phase, in a colloidal gel, the network is built from agglomeration of colloidal particles. In a polymer gel the particles have a polymeric sub-structure made by aggregates of sub-colloidal particles. Generally, the sol particles may interact by vander Waals forces or hydrogen bonds. A gel may also be formed from linking polymer chains. In most gel systems used for materials synthesis, the interactions are of a covalent nature and the gel process is irreversible. A sol consists of a liquid with colloidal particles which are not dissolved, but do not agglomerate or sediment. Agglomeration of small particles are due to vander Waals forces and a tendency to decrease the total surface energy. Vander Waals forces are weak, and extend only for a few nanometers. The gelation process may be reversible if other interactions are involved. The idea behind sol-gel synthesis is to "dissolve" the compound in

a liquid in order to bring it back as a solid in a controlled manner. Multi component compounds may be prepared with a controlled stoichiometry by mixing sols of different compounds. The sol-gel method prevents the problems with co-precipitation, which may be inhomogeneous, be a gelation reaction. Enables mixing at an atomic level. Results in small particles, which are easily sinterable. Sol-gel synthesis may be used to prepare materials with a variety of shapes, such as porous structures, thin fibers, dense powders and thin films.

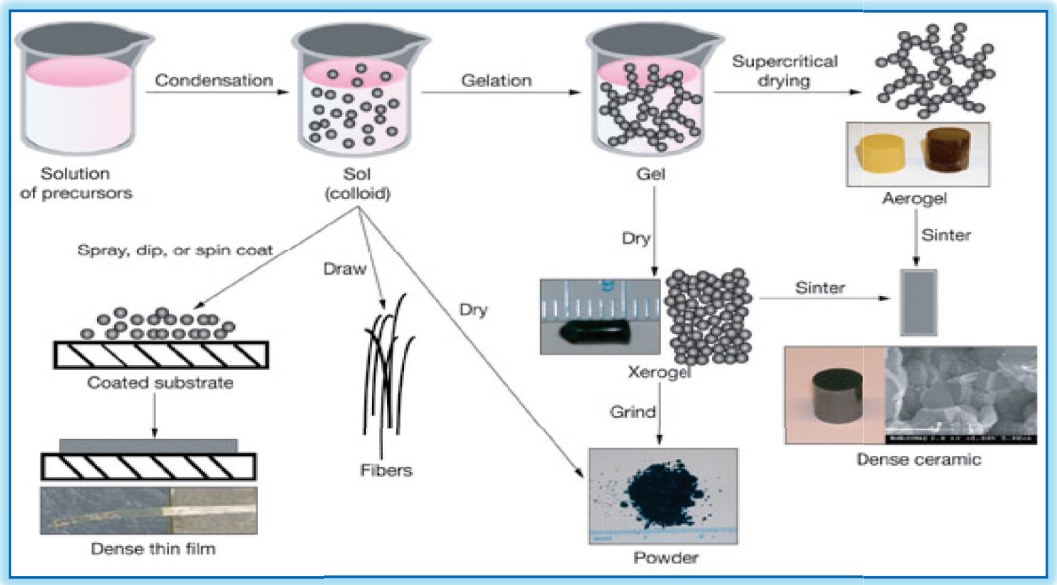


Figure 2: sol –gel process

If the gel is dried by evaporation, then the capillary forces will result in shrinkage, the gel network will collapse, and a xerogel is formed. If drying is performed under supercritical conditions, the network structure may be retained and a gel with large pores may be formed. This is called an aerogel, and the density will be very low. A record is < 0.005 g/cm3.

2. Hydrothermal Method

Hydrothermal synthesis is normally conducted in steel pressure vessels called autoclaves with or without Teflon liners under controlled temperature and/ or pressure with the reaction in aqueous solution. The temperature can be elevated above the boiling point of water, reaching the pressure of vapour saturation. This method is widely used for the production of small particles in the ceramics industry.

The use of Hydrothermal method in preparing metals or metal oxides has become a recent trend. This is because the resultant powder needs no more high-temperature calcinations and thus can avoid the nano-particles from re-clustering and from being contaminated. In the process of preparing nano-powder by hydrothermal method, any of the operating temperature, pressure and reaction path affects the shape and size of the particle.

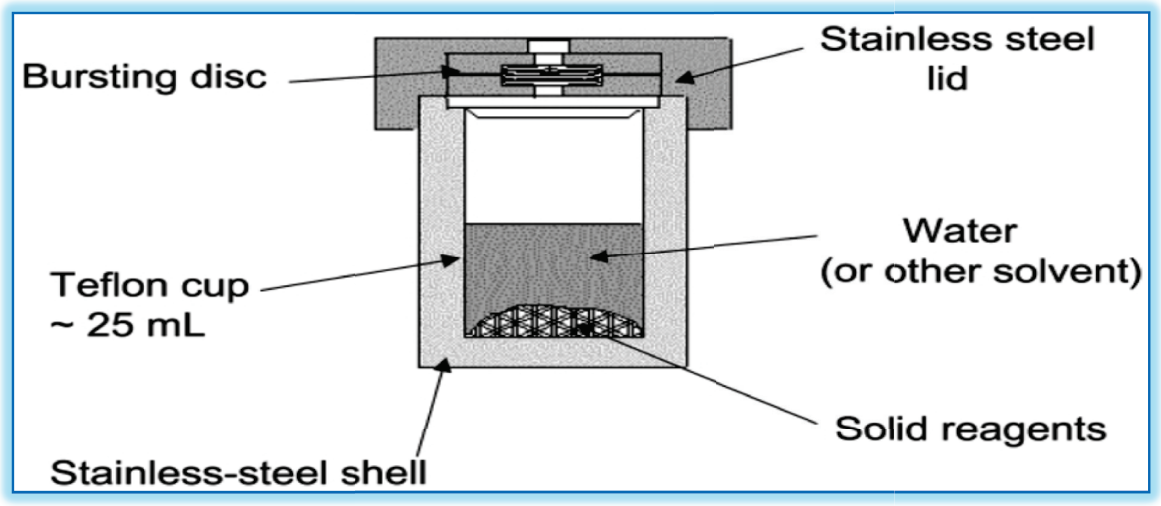


Figure 3: Setup of Hydrothermal process

Advantages of Hydrothermal Method

Does without the high-temperature calcinations process or crushing thus saving much cost on energy. The product are homogeneous in composition, easy to control the purity, composition, size and crystal shape of the powder. Makes it possible for the heating path to avoid transition from meso phasa to sub-state phase.

6.2 Characterization techniques of Nanoparticles

1. X-ray diffraction (XRD)

A very useful and widely used technique for characterizing solid materials is X-ray diffraction (XRD). The technique reveals detailed information about the chemical composition, crystallographic structure, orientation and various defects in a crystalline material. The process of interaction between X-rays and the electrons in a matter is governed by inelastic or elastic scattering. When monochromatic X-rays impinge onto a surface plane of a crystal lattice, some are reflected off the plane with an angle of reflection equal to the angle of incidence, while the rest are transmitted and subsequently reflected by deeper lying crystal planes. The reflected X-rays interfere with each other either constructively or destructively. Constructive interference occurs when two waves are in phase and add together to produce stronger intensity. This condition is shown schematically in fig. 13 for an X-ray with an incident and scattering angle of . The two reflected rays are in phase when the distance ABC, i.e. the difference in distance travelled by the reflected rays from the adjacent planes, is equal to a whole number of wavelengths. From these conditions one can derive Bragg's Law, which is expressed by

$$n\lambda = 2\, d_{hkl} \sin \Theta$$

where n is the order of reflection (n = 1,2,3…), is the wavelength of the X rays,

d is the distance between the planes with the Miller indices (hkl).

The resulting wave interference pattern is the basis of diffraction analysis valid for any beam, e.g. ions, electrons and neutrons, having a wavelength similar to the inter-atomic distance in the lattice.

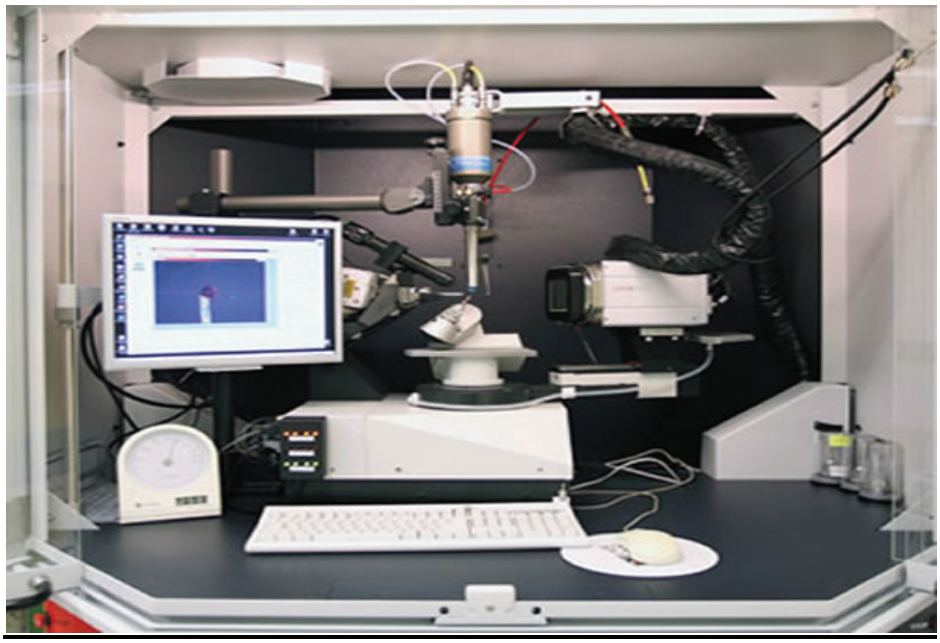


Figure 4 :Digram of XRD

2. Fourier Transform Infrared (FTIR) Spectroscopy

The physics of the individual atoms and simple molecules can be understood by studying their interaction with electromagnetic radiations. This study is called as spectroscopy. In spectroscopy, electromagnetic radiation of a particular frequency or a range of frequencies is allowed to fall on a sample. The radiation coming out of the sample is then analyzed in terms of the intensity at different frequencies. This indicates about the line absorbed or emitted by the molecule, and hence giving a picture of the molecular energy levels.

Here the term FTIR refers to Fourier transform Infrared spectroscopy, when intensity time output of the interferometer is subjected to a Fourier transform to convert it to a familiar infrared spectrum (intensity frequency). The energy of infrared radiation corresponds to the difference of vibrational energy modes in a molecule. Infrared spectroscopy is therefore a probe of vibrational motion of a molecule. The technique works on the fact bonds and groups of bonds vibrate at characteristic frequencies. FTIR analysis provides information about the chemical bonding or molecular structure of materials, whether organic or inorganic.

Figure 5: Picture of Fourier transform Infrared spectrometer

3. Scanning Electron Microscope (SEM)

Scanning electron microscope (SEM) is basically a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern.

The experimental setup is shown in figure3.4. The electron interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity. SEM is used for various purposes like Topographic studies and microstructure analysis, Elemental analysis (if equipped with appropriate detector (energy/wavelength dispersive x-ray). Chemical composition and elemental mapping. In SEM, Primary electron are thermonically or field emitted by a cathode filament (W or LaB) or a filled emission gun (W-tip) and after that accelerated with high energy typically 1-30 KeV. The electron beam is steered with scanning coils over the area of the interest. Upon interaction with material, the primary electrons decelerate as well as losing his energy, transfer it in elastically to other atomic electron and to the lattice.

Figure 6 : Setup of SEM

Due to continuous scattering events the primary beam spread up with different energies depending on source origin as the interaction volume with various electron emitted and their respective energy. Secondary electron (1-50 eV) are mostly used for the imaging the topography and to reproduce the surface. High energy elastically backscattered electrons depends on the atomic number (Z) of the element, which is useful to obtain X-ray characteristic can be used to qualitatively and quantitatively analyze the elemental compostion and distribution in the sample as shown in figure 3.5.

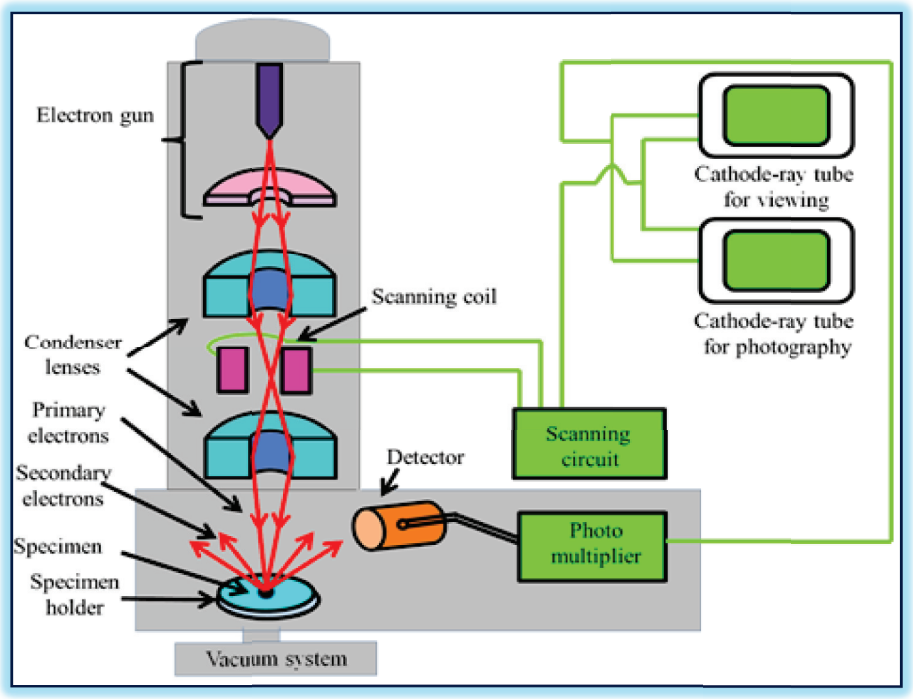


Figure 7: Experimental process of SEM

3.1 SEM setup

The experimental setup consists of an electron gun, column, scanning system, substrate chamber and dectectors.

3.2 Electron gun

It is based on the themal emission. The electron source is commonly a tungsten (W) or lanthanium hexaboride (LaB_6) tip. Electron are emitted during heating.

3.3 Column

The column consist of two electromagnetic lenses acting on the electron beam. The first lens, the condenser lens produces most of the beam demagnification, while the second, objective lens focuses the beam onto the sample. In columns, a beam shaper called stigmator, the stigmator can create a magnetic field around the beam to restore it in a circular cross section.

3.4 Scanning system

To get image on the display the beam should be scanned over the specimen information from any point on the sample can then reproduced in the same relative position on the display.

3.5 Substrate chamber

The substrate holder depends on the different size and shape of the sample. The sample can be moved in three dimensions, as well as rotated and titled

3.6 Detector

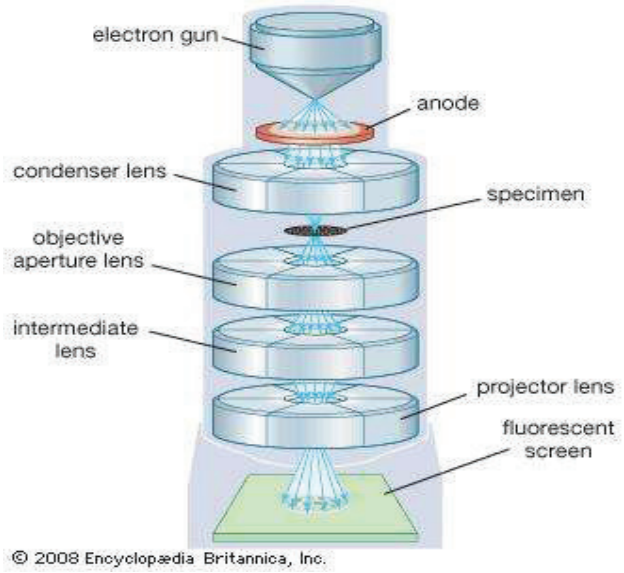
The most detector types used for secondary electrons are the scintillation detector. It can also be used for primary electrons.

3.7 X-ray detector

Spectrometers for detection and analysis of X-ray are based on either of two principles are wavelength dispersive X-ray (WDX); determines the wavelength of the X-rays.Energy dispersive X-ray (EDS); determine the energy of the X-rays.

4. Transmission electron microscope (TEM)

Electron Microscopes are scientific instruments that use a beam of highly energetic electrons to examine objects on a very fine scale. This examination can yield the information like topography, morphology, composition as well as crystallographic information's. Working principle is exactly as their optical counterparts except that they use a focused beam of electrons instead of light to "image" the specimen and gain information as to its structure and composition. The main use of this technique is to examine the specimen structure, composition or properties in sub microscopic details so that this microscopy technique is significantly involved in numerous fields. In TEM there is no change in the refractive index of the medium when the illumination beam is deflected, the vacuum in the lens is the same as the vacuum in the column. Deflection is in this case only due to the electromagnetic properties of the lens which are defined by electromagnetic plates that are only able to influence the path direction of the electrons, since all of the electrons carry a negative charge. Those electrons that pass through the sample go on to form the image while those that are stopped or deflected by dense atoms in the specimen are subtracted from the image.In this way a black and white image is formed. Remaining other electrons which passes close to heavy atom and get only slightly deflected make their way down the column and contribute to the image.. There are three main reasons why the microscope column must be operated under very high vacuum. The first of these is to avoid collisions between electrons of the beam and stray molecules. Such collisions can result in a spreading or diffusing of the beam or more seriously can result in volatization event if the molecule is organic in nature. Such volatizations can severely contaminate the microscope column especially in finely machined regions such as apertures and pole pieces that will serve to degrade the image.



Figures 8 :Diagram of TEM

5. UV-Vis Spectroscopy

Ultraviolet Visible Near-Infra red (UV-Vis-NIR) spectroscopy is useful to characterize the absorption, transmission, and reflectivity of a variety of technologically important materials, such as pigments, coatings, windows, and filters. This more qualitative application usually requires recording at least a portion of the spectrum for characterization of the optical or electronic properties of materials. Absorbance spectroscopy, commonly referred to as spectroscopy, is the analytical technique based on measuring the amount of light absorbed by a sample at a given wavelength. Spectroscopy, particularly in the visible and UV portions of the electromagnetic spectrum, is one of the most versatile and widely used techniques in chemistry and the life sciences. Molecular absorption spectroscopy in the ultraviolet (UV) and visible (VIS) is concerned with the measured absorption of radiation in its passage through a gas, a liquid or a solid. The wavelength region generally used is from 190 to about 1000nm, and the absorbing medium is at room temperature. Ultraviolet-visible spectroscopy (UV-Vis) refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible spectral region. UV-Vis absorption spectroscopy measures the percentage of radiation that is absorbed at each wavelength. Typically this is does by scanning the wavelength range and recording the absorbance. It is widely used in organic chemistry to investigate the extent of multiple bond or aromatic conjugation within molecules. The technique can be expended to gases and solids, and also beyond absorption, to include measure reflected rather than transmitted light.It is also used for the measurement of electronic band gap of semiconductor films

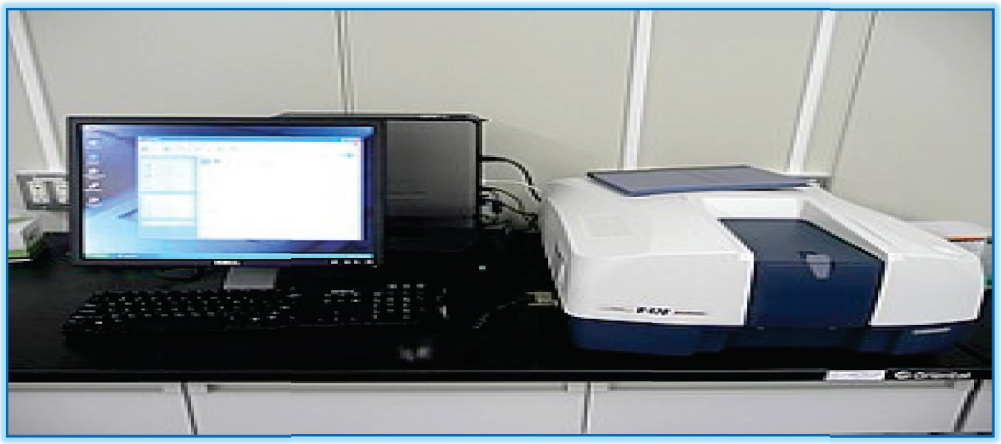


Figure 9: UV-Visible Spectrometer instrument, UV800

UV-Vis refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet - visible spectral region. This means it uses light in the visible and adjacent (near-UV and near-infrared [NIR] ranges. The absorption or reflectance in the visible range directly affects the perceived colour of the chemicals involved. In this region of the electromagnetic spectrum, molecules undergo electronic transitions.

This technique is complementary to fluorescence spectroscopy, in that fluorescence deals with transitions from the excited state to the ground state, while absorption measures transitions from the ground state to the excited state

Band gap energy is calculated using the relationship of photon energy and frequency

$$E_g = hc/\lambda$$

where h is the Planck's constant ($6.626*10^{-34}$Js), c is the speed of light ($2.998*10^{8}$m/s) and λ is the wavelength of light.

6. Vibrating Sample Magnetometer

MicroSense VSMs are the easiest to use vibrating sample magnetometers with the widest range of options available. Whether you are measuring magnetic moment and coercivity of thin films or studying the magnetic properties of liquids, powders, or bulk samples, the VSMs will give you the easiest and most accurate magnetic measurements. The magnetic properties of solids are very important, and attempts to understand them have led to a deep insight into the fundamental structure of many solids, both metallic and non-metallic. The VSM is the instrument used to measure the magnetic moment, the most fundamental quantity in magnetism, of solid samples.When a sample material is placed in uniform magnetic field, a dipole moment proportional to the product of sample susceptibility and applied field is induced in the sample.If the sample is made to undergo sinusoidal motion as well, an electrical signal will be induced in suitable located stationary pick-coils. This signal, which is at the vibration frequency, is proportional to the magnetic moment, vibration amplitude and vibration frequency. The instrument displays the magnetic moment in e.m.u. units.

Specifications:
1.Range: 0.00001 to 10000 e.m.u.
2.Magnetic field :-10 to +10 kOe
3.Temperature range : 77 to 1050 K

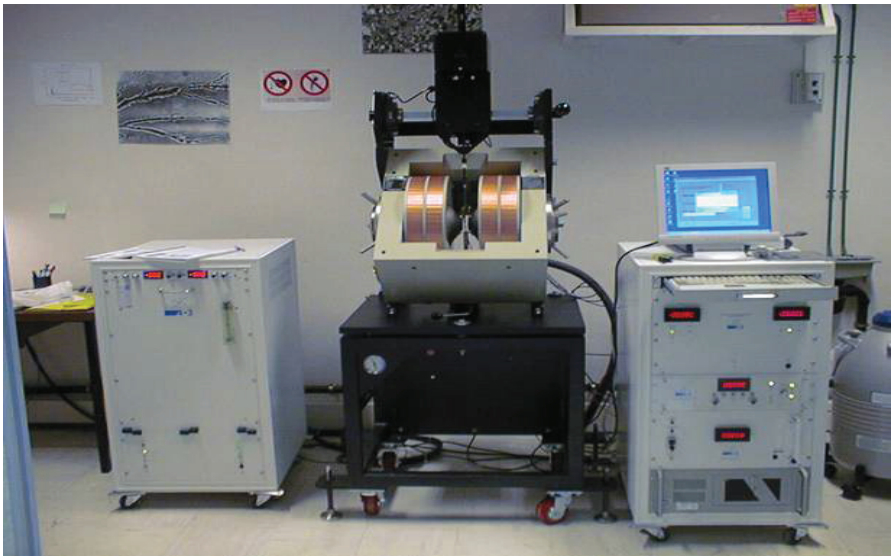


Figure 10:Diagram of VSM

7. Plan Of Work

Timeline/Research Planning – an outline of the timescale of the research, indicating how long different tasks are envisaged to take, and the sequence of different task in the time available is given below :

- Three months, to review literature and learn of sol-gel and hydrothermal methods for synthesis of materials.
- In next six months, the different structural phases of NiO will be synthesize by sol-gel and hydrothermal method and calcinate them at different temperature to get a low dimension varities of shaped with controlled morphology (-Nps, -wires, -flakes etc.) and size (1-100 nm) and characterize the samples by different techniques (XRD, SEM, TEM, UV-Vis, FTIR, VSM)
- Meanwhile, we will publish the results in conferences and journals.
- In next six months, we will synthesized Fe_2O_3 by sol-gel and hydrothermal method with varying calcinations temperature To get different phases will change the calcinations temperature and characterize the samples by different techniques.
- Then, we will publish the results in conferences and journals.
- Next, three months we compare the properties of the above samples obtain from both the synthesis method.
- Keeping the view of above study we will see these material impact on human and environmental health particularly for the heavy metal ions in purification of water.

References

1. A. Mirzaei, K. Janghorban, B. Hashemi, S. R. Hosseini, M. Bonyani, S. G. Leonardi, A. Bonavita, G. Neri (2016). Synthesis and characterization of mesoporous Fe_2O_3 nanoparticles and investigation of electrical properties of fabricated thick films. *Processing and Application of Ceramics*,**10**, 209–217.
2. A. Rahdar, M. Aliahmadb, Y. Azizib (2015), *Journals of Nanostruct*., **5**, 145-151.
3. A. M. Soleimanpour and A. H. Jayatissa (2012), *Materials Science and Engineering*, **32**, 2230–2234.
4. A. K. Bandyopadhyay (2008), *Nano Materials: in Architecture, Interior Architecture and Design, New Age International, New Delhi*.
5. C. N. R. Rao, A. Muller, A. K. Cheetham (2004), *The Chemistry of Nanomaterials: Synthesis, Properties and Applications Willey*, **135**
6. D.C. Coffey and D. S. Ginger(2006), **5**, 735.
7. H. S. Nalwa(2000), *Handbook of nanostructured materials and nanotechnology*, Academic Press.
8. H. E. L. Hernandez, C. S. Perez, A. G. J. Valenzuela (2010), *Opt. A: Pure Appl.* **10**.
9. K.R Sharma , S. Thakur ans N.S Negi (2018). Synthesis and Characterization of NiO paticles annealed at different temperature. *AIP conference proceedings,* **1942**, 12011.
10. L.Chacka and P.M Aneesh (2018). Effect of growth techniques on the structural and Optical properties of TiO_2 nanostructures. *Material Research Express,* **5**, 1.
11. M.S. Lasoued, S. Garcia- Granda, B. Dkhil, S.Ammar and A. Gadri. Synthesis and Characterization of Ni doped Fe_2O_3 nanoparticles through precipation with enhanced photocatalytic activities(2018). *Journals of mater.sci:materials in Electronics*, **29**, 5726-5737.
12. M. Kavitha and C.Gopinathan and P.Pandi (2013). Synthesis and Characterization of TiO_2 Nanopowders in Hydrothermal and Sol-Gel Method. *Internat. Jour. of Advance. in Research & Tech.*, **2**, 102-108.
13. M. Jlassi, M. Kandyla (2015). *Journal of Alloys and Compounds*, **626**, 87–92.
14. M. Muccini (2006), *Nature Materials,* **5,** 605.
15. R. Vijayalakshmi and V. Rajendran (2012).Synthesis and characterization of nano-Tio2 via different methods. *Arch. of Applied Sci. Research***,4**,1183-1190.
16. R. Riasat and G. Nie (2016), *Journal of Nanomat*., 1-7.
17. S. R. Khan, S.Jamil, M.R Saeed, A. Janjua and R.A khera (2017). Synthesis of ferric Oxyhydrides nanoparticles and ferric oxides nanorods by reflux assisted co-orecipitation method and comparative study of their thermal properties, **4**, 11 .
18. S Basvaraja, D.S balaji, M. D bedra, D Raghunandan, P. M prithviraj swany and A Venkataraman (2011). Solvothermal synthesis and characterization of acicular α -Fe2O3 nanoparticles, *Bull. Mater. Sci*. **34**, 1313–1317.
19. S. Valencia, J. M. Marín and G. Restrepo (2010), *The Open Materials Science Journal*, **4**, 9-14.

20. T. T. Le Dang, M. Tonezzer and V. H Nguyen (2015). Hydrothermal Growth and Hydrogen Selective Sensing of Nickel Oxide Nanowires. *Journal of Nanomaterials*, **2015**, 1-8.
21. U. Ashraf and B. Khan (2015).Synthesis and Characterization of NiO Nanopowder by Sol-Gel Method. *Internat. Journal of Sci. and Research*,**4**, 2405-2408.
22. W. Qin, C. Y. Ran Yi and U. Gao(2010). Hydrothermal Synthesis and Characterization of Single-Crystalline α-Fe_2O_3 Nanocubes. *Journal of Nanomaterials*,**2011**, 1-6.
23. X. Sun, H. Liu, J. Dong, J. Wei, Y. Zhang (2010) , *Catal. Lett*.,**135**, 219.
24. Y. Li and J. Shi (2014), *Advanced Materials*, **26**,3176–3205.
25. Z. Wang, Z.Wang, H. Wu, and X. W. Lou (2013), *Scientific Reports*, **3**, 1391.